Electronic Supplementary Information

Water Desalination through Rim Functionalized Carbon Nanotubes

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1. Effects of Membrane Thickness on Water Flux and Salt Rejection

To examine effects of membrane thickness, (9,9) CNTs with four different lengths are built and studied. As shown in ESI Fig. S1, both water flux and salt rejection remain close to a constant with increasing the membrane thickness. Since salt-ion transport is mainly affected by the energy barrier at the CNT entrance, as long as the pore rim condition remains the same, the salt rejection will not change too much with the membrane thickness. As for the water flow in CNTs with the sub-nm diameter, pervious theoretical and experimental works have shown that water molecules are confined into a single-file within the channel of CNTs.[1-3] Such a channel leads to a narrow distribution of interaction energy and lowers the free energy. This unique phenomenon allows super-fast water flow in the CNTs and thus, the small difference in the membrane thickness has negligible impact on the water flux.

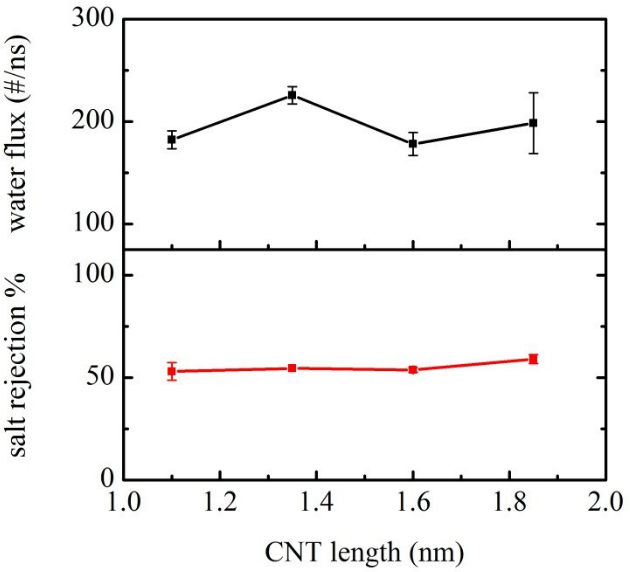

Figure S1. The water flux and salt rejection versus the membrane thickness for (9,9) CNTs with zero rim dipole moment and under 800 MPa external pressure.

2. Interatomic Potentials

The pairwise interactions among atoms of CNT, water and ions are described by the 12-6 Lennard-Johns (LJ) potential with or without the Coulombic interaction term. The parameters used in this paper are summarized in Table S1, where σ and ε are the energy and distance parameters in the LJ potential, and q represents the charge in Coulombic term.[4-6] Originally, the charge of $\mathrm{C_{CH}}$ (Q_C) is −0.115e, while the charge of $\mathrm{H_{CH}}$ (Q_H) atoms is +0.115e, as shown in Table S1 with underline. For later modelling, Q_C is modified from −0.515e to +0.515e, and Q_H is changed from +0.515e to −0.515e accordingly.

Table S1. Lennard-Jones potential and charge parameters used in this work.

Element	**C (sp2)**	**$\mathrm{C_{CH}}$**	**$\mathrm{H_{CH}}$**	**$\mathrm{H_w}$**	**$\mathrm{O_w}$**	**$\mathrm{Cl^-}$**	**$\mathrm{Na^+}$**
ε (kcal/mol)	0.0859	0.046	0.0301	0	0.16275	0.0117	0.1684
σ (Å)	3.3997	2.985	2.42	0	3.16435	5.1645	2.2589
Q (e)	0	**−0.115**	**+0.115**	0.5242	−1.0484	−1	1

3. Osmotic Pressure Estimation

The osmotic pressure can be estimated by

$$\Pi = cRT \, , \tag{S1}$$

where R is the gas constant, T is the temperature and c is the molar concentration of NaCl in the permeate side, given by $c = N_{salt} / N_A V$. Here, N_A is the Avogadro constant, N_{salt} is the number of salt ion in the permeate side solution with volume V, where $V = N_{H_2O} M_{H_2O} / N_A D_{H_2O}$. Here, N_{H_2O}

is the number of water molecules in the permeate side, M_{H_2O} is the molar mass of water molecule, and D_{H_2O} is the density of water solution. Thus, the Eq. S1 becomes

$$\Pi = N_{salt} D_{H_2O} RT / N_{H_2O} M_{H_2O} . \tag{S2}$$

During the simultion, the volume of the solution and the number of salt ions in the solution change with time. We can use the initial concentration of the salt solution $c = 123 \text{ g} / \text{L}$ to estimate the value of osmotic pressure $\Pi = cRT = 5.25 MPa$.

4. Water Flux and Salt Rejection Results Summary

For (9,9) and (7,7) CNTs, the water flux versus external pressure at different rim charge Q_C is shown in Fig. S2, while the salt rejection results are presented in Fig. S3.

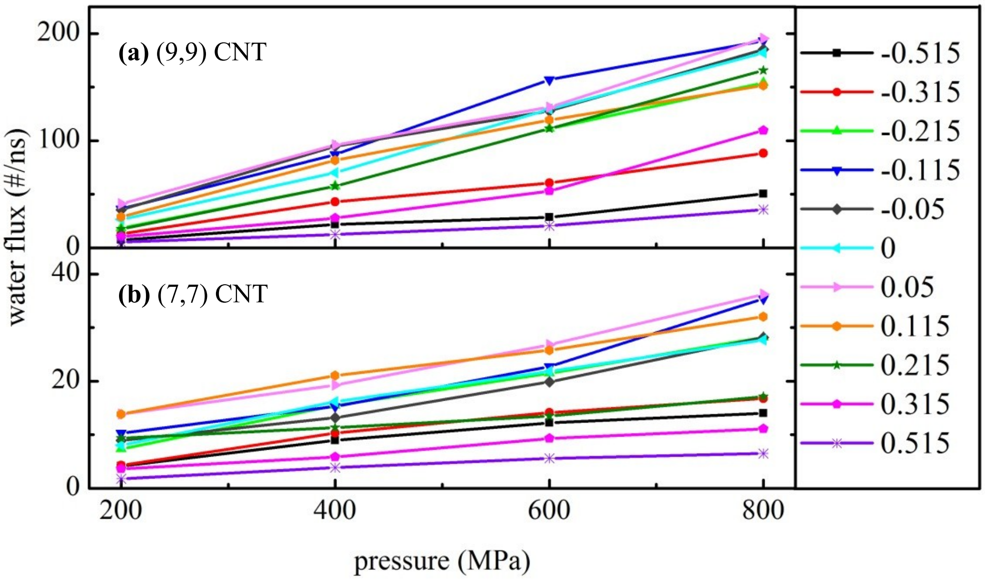

Figure S2: Water fluxes for a) (9,9) and b) (7,7) CNTs versus extermnal pressure for CNT rim charge varying from –0.515 e to 0.515 e.

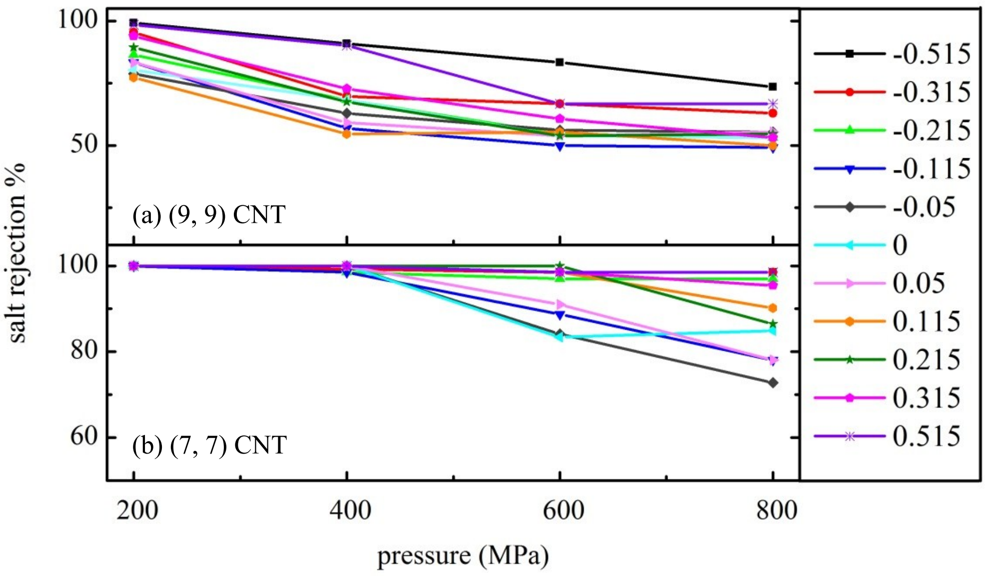

Figure S3: Salt rejection rates for a) (9,9) and b) (7,7) CNTs versus external pressure for CNT rim charge varying from −0.515e to 0.515e.

5. Potential of Mean Force for Water Molecules in (9,9) CNTs

We also compute the PMFs of water molecules in (9,9) CNTs with different dipole moment as shown in Fig. S4. Regardless of the CNT charges, the water transport always encounters an energy barriers < 0.7 kcal/mol.

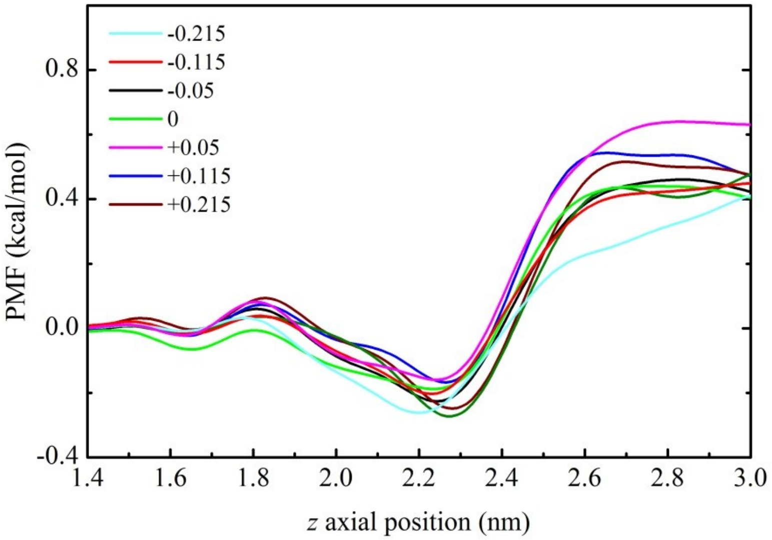

Figure S4: PMFs of moving a single water molecule through differently charged (9,9) CNTs.

6. Potential of Mean Force for Cl⁻ Ion in (9,9) CNT with Different Dipole Moment Density

The original (9,9) CNT rims are passivated by 9 hydrogen atoms. To evaluate the effects of dipole moment density on the PMFs, two hydrogen atoms are randomly removed from the (9,9) CNT rim. The PMF of moving a single Cl^- ion through (9,9) CNT with $Q_C = 0$ and -0.515e is calculated in both 7 and 9 hydrogen atoms cases. The results are summarized in Fig. S5.

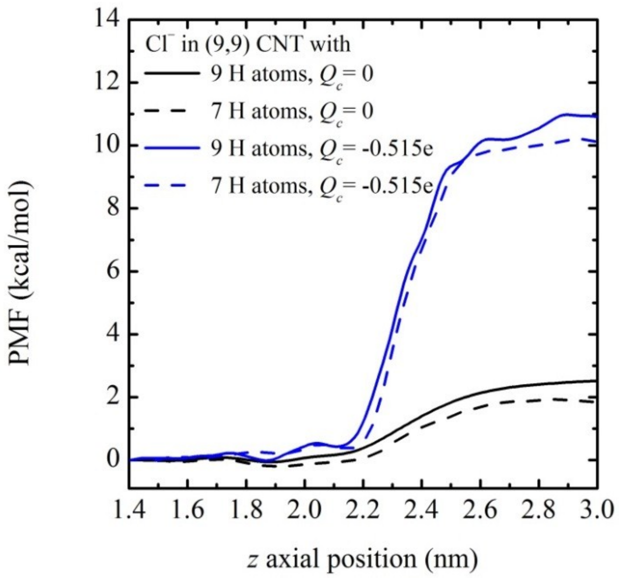

Figure S5. PMFs of moving a Cl$^-$ ion through (9,9) CNT with different dipole moment and density.

7. Radial Distribution Function (RDF) Example

Radial distribution function is computed by counting the occurrence probabilities of water molecules in the vicinity of a single salt ion. A series of RDFs along the z axis are calculated, covering the entire CNT length. An RDF example is shown in Fig. S6.

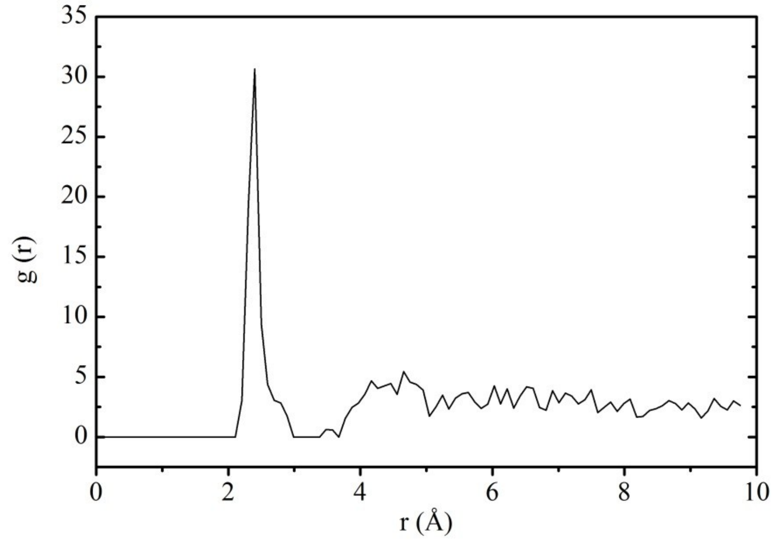

Figure S6. Computed RDF between water molecules and an Na^+ ion in (9,9) CNT.

SUPPORTING REFERENCE

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